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(54) **Low pH granular laundry detergent compositions containing aluminosilicate citric acid and carbonate builders**

Niedrig-pH-Waschmittelgranulate enthaltend Aluminiumsilikat, Zitronensäure und Carbonatbuilder

Compositions détergentes granulaires pour le linge ayant un pH bas et contenant des renforceurs d'aluminosilicate, d'acide citrique et de carbonate

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EP-A- 0 220 024 EP-A- 0 313 143
EP-A- 0 326 208 GB-A- 2 106 482
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EP 0 456 315 B1

Description**Technical Field**

5 The present invention relates to low pH, granular laundry detergent compositions. Certain preferred compositions herein contain a low level of a chlorine scavenger, preferably an ammonium salt. The compositions minimize fading of fabric colors sensitive to higher wash water pHs and to the low levels of chlorine present in the wash and rinse water. Other preferred compositions herein are dense, low or no phosphate detergents containing a specific aluminosilicate, citric acid and carbonate builder system. These compositions provide good cleaning performance while maintaining
10 good physical properties.

Background Art

15 Granular laundry detergents typically are formulated to provide a wash water pH of about 9.8 to 10.5. This pH range can cause fading of some fabric dyes after multiple laundry cycles. When the wash solution is diluted in the rinse, the pH is lowered to a range of about 7 to 9 where some fabric dyes are generally less sensitive to pH.

Chlorine is used in many parts of the world to purify water. To make sure that the water is safe, a small residual amount, typically about 1 part per million (ppm), of chlorine is left in the water. It has been found that even this small amount of chlorine can cause fading of chlorine-sensitive fabric dyes. In a typical wash, there is usually enough soil
20 on the fabrics to scavenge residual chlorine and minimize damage to chlorine-sensitive dyes. However, in the rinse the soil levels are greatly reduced, as is the pH, and chlorine-sensitive dyes can fade after multiple laundering cycles. Chlorine is also more aggressive to dyes at the lower pHs. Thus, fading of fabric colors over time is a result of both the high pH of typical granular laundry detergents and the presence of residual chlorine in the wash and rinse water.

Delivering good cleaning performance from a low or no phosphate condensed detergent is difficult due to limitations
25 in conventional spray dry processing. Additionally, trying to compensate with higher levels of actives (surfactant and builder) is limited without significantly diminishing product physical properties (solubility, lumping/caking, scoopability).

Summary of the Invention

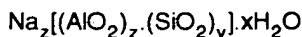
30 The present invention encompasses granular laundry detergent compositions comprising, by weight:

(a) from 15% to 25% of a mixture of a C₁₁-C₁₃ alkylbenzene sulfonate surfactant and a C₁₂-C₁₆ alkyl sulfate surfactant in a weight ratio of sulfonate surfactant to sulfate surfactant of from 4:1 to 1:1;

(b) from 1% to 3% of an alkali metal silicate having a molar ratio of SiO₂ to alkali metal oxide of from 1.0 to 2.4;

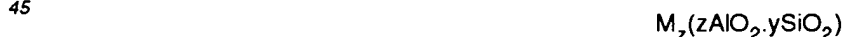
35 (c) from 20% to 30% of a finely divided aluminosilicate ion exchange material selected from the group consisting of:

(i) crystalline aluminosilicate material of the formula:



40 wherein z and y are at least 6, the molar ratio of z to y is from 1.0 to 0.5 and x is from 10 to 264, said material having a particle size diameter of from 0.1 micron to 10 microns, a calcium ion exchange capacity of at least about 200 mg CaCO₃ eq./g and a calcium ion exchange rate of at least 0.130 g/l/min/g/l (2 grains Ca⁺⁺/gallon/minute/gram/gallon);

(ii) amorphous hydrated aluminosilicate material of the empirical formula:



45 wherein M is sodium, potassium, ammonium, or substituted ammonium, z is from 0.5 to 2 and y is 1, said material having a magnesium ion exchange ion exchange capacity of at least 50 milligram equivalents of CaCO₃ hardness per gram of anhydrous aluminosilicate and a Mg⁺⁺ exchange rate of at least 0.065 g/l/min/g/l (1 grain/gallon/minute/gram/gallon); and

(iii) mixtures thereof;

(d) from 4% to 10% of citric acid;

55 (e) from 5% to 20% of an alkali metal carbonate; said composition having a pH of from 7 to 9.3 at a concentration of 1% by weight in water at 20°C, and said composition having a density of from 500 to 600 grams per liter.

Preferably, the present compositions also contain a chlorine scavenger employed in an effective amount to control residual chlorine in the wash and rinse water. The amount of chlorine scavenging material needed will vary, but only

a small amount is used to avoid destroying hypochlorite bleach that may be added deliberately to treat bleach-sensitive stains.

Detailed Description of the Invention

The granular laundry detergent compositions of the present invention are formulated to provide a pH of from 7 to 9.3, preferably from 8 to 9.1, more preferably from 8.5 to 9.0, at a concentration of 1% by weight in water at 20°C. The individual components of the compositions herein are described in detail below.

Chlorine Scavenger

When present in the compositions of the invention chlorine scavengers should not be used in a large excess since they will interfere with normal hypochlorite bleaches added to the wash water for stain removal and whitening. The level should be from 0.01% to 10%, preferably from 0.05% to 5%, most preferably from 0.08 to 2%, based on the molar amount equivalent to react with 0.5 to 2.5, typically about 1, ppm of available chlorine, per average rinse. If both the cation and the anion of the scavenger react with chlorine, which is desirable, the level is adjusted to react with an equivalent amount of available chlorine.

Suitable chlorine scavengers include the following polymers which can be divided into four groups according to their structural construction: polyethyleneimines, polyamines, polyamineamides and polyacrylamides, of which the polyethyleneimines, the polyamines and polyamineamides are especially preferred.

Suitable polyethyleneimines are obtained by acid-catalyzed polymerization of ethyleneimine and can be modified by urea and epichlorhydrin or dichlorethane. Polyethyleneimines can contain primary, secondary or tertiary amino groups as well as quaternary ammonium groups. Aqueous solutions of polyethyleneimines show basic reaction. The molecular weight can amount up to about 1,000,000.

Polyamines are addition or condensation products from multivalent aliphatic amines and compounds with several groups capable of reacting, for example, epichlorhydrin or alkylene dihalides. Therefore, they always contain several secondary, tertiary or even quaternary nitrogen atoms, as well as eventually also hydroxyl groups in the molecule. They are accordingly hydrophilic, polar compounds, which behave as polyelectrolytes and are water soluble, inasmuch as they do not contain large hydrophobic groups in the molecule. The polyamines exhibit basic reaction in aqueous solution. Suitable compounds, for example, are described in U.S. Patent 2,969,302.

Polyamineamides contain amino- and amido groups in the molecule at the same time. They are made, for example, by condensation of multibasic acids, for example, dibasic, saturated, aliphatic C₃ to C₈ acids and polyamines, as well as with compounds, which contain several groups capable of reacting, such as, for example, epichlorhydrin. These compounds also demonstrate basic reaction in aqueous solution. Suitable polyamineamides are described, for example, in U.S. Patent 2,926,154.

Polyacrylamides having amino groups and molecular weights up to several million are suitable for use herein. By building in carboxyl groups, which are formed, for example, by partial hydrolysis, anionic polyacrylamides are obtained in addition to amido groups, while polyacrylamides containing amino groups exhibit basic reaction in aqueous solution. Amino groups can be introduced, for example, by reaction with alkali and hypobromite or hypochlorite.

It is common to all polymers that they are water soluble. Such polymers are commercial products. Compounds especially well suited as inserts to the detergents conforming to the discovery are the polyethyleneimines and polyamines, which exhibit strong basic reaction in water. Examples of commercially available polyethyleneimines, which are particularly appropriate, are "Epomin SP-003" from Nippon Shokubai, "Lugalvan G20 and G35" from BASF, and "Ethyleneamine E-100" from Dow Chemical. These polymers can be added either alone or together with water soluble polymers from melamine or urea and formaldehyde. Other polymers suitable for the detergents conforming to the discovery are, for example, the water soluble polymers based on alkyleneimines, acrylamides as well as melamine or urea and formaldehyde, which are described in the "Encyclopedia of Polymer Science and Technology, John Wiley & Sons, Inc., New York, 1968, Vol. 9, p. 762. An addition of these polymers to the detergents conforming to the discovery in combination with the amino- and/or amido group-containing polymers causes an intensification of the dye-protective effect.

Preferred polymers for use in the preferred anionic surfactant containing compositions herein are polyethyleneimines. Polyethyleneimines are believed to be particularly efficient chlorine scavengers because they adsorb to cotton fibers. In an anionic surfactant matrix, ion pairing of the amines with surfactant or polymeric carboxylates tends to dramatically lower the solubility of the polymeric amine. The solubility of the polymeric amine complexes can be maintained by utilizing materials of relatively low molecular weight. The molecular weight of the chosen amine polymer should be controlled to achieve a fabric substantivity of preferably at least 50%. A low substantivity will not allow efficient carryover into the rinse. Preferred polyethyleneimines have a molecular weight of less than 800, more preferably from 200 to 400.

The cationic charge and the solubility of the polymeric amine allow the deposition of the polymer onto cotton fabric. The affinity the polymer has for fabric increases with lower pH, or higher molecular weight. Thus, a balance of these properties (solubility, solution pH, and polymer molecular weight) controls the efficiency of the chlorine scavenger on fabric and in solution. The optimal composition will allow a balance of polymer on fabric (for carryover from wash to rinse) and in solution (for an efficiency rate of reaction with chlorine).

Other chlorine scavengers herein are anions selected from the group consisting of reducing materials like sulfite, bisulfite, thiosulfite, thiosulfate, iodide, or nitrite and antioxidants like carbamate, or ascorbate, and mixtures thereof. Conventional non-chlorine scavenging anions like sulfate, bisulfate, carbonate, bicarbonate, nitrate, chloride, borate, phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, or salicylate and mixtures thereof can be used with ammonium cations.

Other chlorine scavengers useful herein include ammonium sulfate (preferred), and primary and secondary amines of low volatility such as ethanolamines, amino acids and their salts, polyamino acids and their salts, fatty amines, glucoseamine and other aminated sugars. Specific examples include tris(hydroxymethyl) aminomethane, monoethanol amine, diethanol amine, sarcosine, glycine, iminodiacetic acid, lysine, ethylenediamine diacetic acid, 2,2,6,6-tetramethyl piperinol, and 2,2,6,6-tetramethyl piperinone.

Other chlorine scavengers include phenol, phenol sulfonate, 2,2-biphenol, tiron, and t-butyl hydroquinone. Preferred are meta-polyphenols such as resorcinol, resorcinol monoacetate, 2,4-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid, and 2,4-dihydroxyacetophenone.

Peroxide bleach sources, e.g. perborate, percarbonate and other persalts, can also be used in minor amounts (less than 3% by weight, preferably less than 2%) as a chlorine scavenger herein. However, peroxides are not efficient chlorine scavengers because they cannot be used at high enough levels to carry over to the rinse water without risk of bleach damage to colors.

Detergent compositions comprising the chlorine scavenger and the detergent component can be provided having various ratios and proportions of these two materials. Of course, the amount of the chlorine scavenger can be varied, depending upon the level of residual chlorine expected by the formulator. Moreover, the amount of detergent component can be varied to provide either heavy-duty or light-duty products, as desired. This invention relates primarily to detergent compositions that contain essentially no additional ingredients which are chlorine scavengers. For example, the other materials present should not provide any substantial additional amounts of ammonium cations in the wash solution.

Detergent Additives

The amount of the detergent surfactant component can, as noted hereinabove, vary over a wide range which depends on the desires of the user. In general, the compositions contain from 5% to 50%, preferably from 10% to 30% by weight, of detergent surfactant, which preferably is an anionic surfactant.

The detergent compositions of the instant invention can contain all manner of organic, water-soluble detergent surfactant compounds. A typical listing of the classes and species of detergent compounds useful herein appear in U. S. Patent 3,664,961. The following list of detergent compounds and mixtures which can be used in the instant compositions is representative of such materials, but is not intended to be limiting.

Water-soluble salts of the higher fatty acids, i.e., "soaps", are useful as the detergent component of the composition herein. This class of detergents includes ordinary alkali metal soaps such as the sodium, potassium, salts of higher fatty acids containing from 8 to 24 carbon atoms and preferably from 10 to 20 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Another class of detergents includes water-soluble salts, particularly the alkali metal salts of organic sulfuric reaction products having in their molecular structure an alkyl group containing from 8 to 22 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic detergents which form a part of the detergent compositions of the present invention are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) produced by reducing the glycerides of tallow or coconut oil; and sodium and potassium alkylbenzene sulfonates, in which the alkyl group contains from 9 to 15 carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in United States Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average of the alkyl groups is about 12 carbon atoms, abbreviated as C₁₂ LAS.

Other anionic detergent surfactant compounds herein include the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; and sodium or potassium salts of alkyl phenol ethylene oxide ether sulfate containing from 1 to 10 units of ethylene oxide per molecule and wherein the alkyl groups contain 8 to 13 carbon atoms.

Water-soluble nonionic synthetic detergent surfactants are also useful as the detergent component of the instant

composition. Such nonionic detergent materials can be broadly defined as compounds produced by the condensation of ethylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

For example, a well-known class of nonionic synthetic detergents is made available on the market under the trade name of "Pluronic". These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. Other suitable nonionic synthetic detergents include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from 6 to 13 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from 4 to 15 moles of ethylene oxide per mole of alkyl phenol.

The water-soluble condensation products of aliphatic alcohols having from 8 to 22 carbon atoms, in either straight chain or branched configuration, with ethylene oxide, e.g., a coconut alcohol-ethylene oxide condensate having from 3 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms, are also useful nonionic detergents herein.

Semi-polar nonionic detergent surfactants include water-soluble amine oxides containing one alkyl moiety of from 10 to 20 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; water-soluble phosphine oxide detergents containing one alkyl moiety of from 10 to 20 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; and water-soluble sulfoxide detergents containing one alkyl or hydroxyalkyl moiety of from 10 to 20 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from 1 to 3 carbon atoms.

Ampholytic detergent surfactants include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

Zwitterionic detergent surfactants include derivatives of aliphatic quaternary ammonium, phosphonium and sulfonium compounds in which the aliphatic moieties can be straight chain or branched, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water-solubilizing group. The quaternary compounds, themselves, e.g. cetyltrimethyl ammonium bromide, can also be used herein.

Other useful detergent surfactant compounds herein include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from 6 to 20 carbon atoms in the fatty acid group and from 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from 2 to 9 carbon atoms in the acyl group and from 9 to 20 carbon atoms in the alkane moiety; alkyl ether sulfates containing from 10 to 20 carbon atoms in the alkyl group and from 1 to 12 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from 12 to 20 carbon atoms; and beta-alkyloxy alkane sulfonates containing from 1 to 3 carbon atoms in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety.

Preferred water-soluble organic detergent compounds herein include linear alkylbenzene sulfonates containing from 11 to 13 carbon atoms in the alkyl group; C₁₀₋₁₈ alkyl sulfates; the C₁₀₋₁₆ alkyl glyceryl sulfonates; C₁₀₋₁₈ alkyl ether sulfates, especially wherein the alkyl moiety contains from 14 to 18 carbon atoms and wherein the average degree of ethoxylation between 1 and 6; C₁₀₋₁₈ alkyl dimethyl amine oxides, especially wherein the alkyl group contains from 11 to 16 carbon atoms; alkyldimethyl ammonio propane sulfonates and alkyldimethyl ammonio hydroxy propane sulfonates wherein the alkyl group in both types contains from 14 to 18 carbon atoms; soaps, as hereinabove defined; and the condensation product of C₁₀₋₁₈ fatty alcohols with from 3 to 15 moles of ethylene oxides.

Specific preferred detergents for use herein include: sodium linear C₁₀₋₁₃ alkylbenzene sulfonates; sodium C₁₂₋₁₈ alkyl sulfates; sodium salts of sulfated condensation product of C₁₂₋₁₈ alcohols with from 1 to 3 moles of ethylene oxide; the condensation product of a C₁₀₋₁₈ fatty alcohols with from 4 to 10 moles of ethylene oxide; and the water-soluble sodium and potassium salts of higher fatty acids containing from 10 to 18 carbon atoms.

It is to be recognized that any of the foregoing detergents can be used separately herein, or as mixtures. Examples of preferred detergent mixtures herein are as follows.

An especially preferred alkyl ether sulfate detergent component of the instant compositions is a mixture of alkyl ether sulfates, said mixture having an average (arithmetic mean) carbon chain length within the range of from 12 to 16 carbon atoms, preferably from 14 to 15 carbon atoms, and an average (arithmetic mean) degree of ethoxylation of from 1 to 4 moles of ethylene oxide, preferably from 1 to 3 moles of ethylene oxide.

The detergent compositions of the present invention can contain, in addition to the detergent surfactant, water-soluble or water-insoluble builders such as those commonly taught for use in detergent compositions. Such auxiliary builders can be employed to sequester hardness ions and to help adjust the pH of the laundering liquor. Such builders

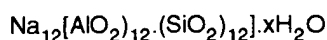
can be employed in concentrations of from 5% to 95% by weight, preferably from 10% to 50% by weight, of the detergent compositions herein to provide their builder and pH-controlling functions. The builders herein include any of the conventional inorganic and organic water-soluble builder salts.

Such builders can be, for example, water-soluble salts of phosphates including tripolyphosphates, pyrophosphates, orthophosphates, higher polyphosphates, carbonates, silicates, and organic polycarboxylates. Specific preferred examples of inorganic phosphate builders include sodium and potassium tripolyphosphates and pyrophosphates.

Nonphosphorus-containing materials can also be selected for use herein as builders.

Specific examples of nonphosphorus, inorganic detergent builder ingredients include water-soluble inorganic carbonate, bicarbonate, and silicate salts. The alkali metal, e.g., sodium and potassium, carbonates, bicarbonates, and silicates are particularly useful herein.

Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available. The aluminosilicates useful in this invention can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in U.S. Pat. No. 3,985,669, Krummel et al, issued Oct. 12, 1976, incorporated herein by reference. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material is Zeolite A and has the formula



wherein x is from 20 to 30, especially 27.

Water-soluble, organic builders are also useful herein. For example, the alkali metal, polycarboxylates are useful in the present compositions. Specific examples of the polycarboxylate builder salts include sodium and potassium, salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acid, polyacrylic acid, polymaleic acid, and citric acid.

Other desirable polycarboxylate builders are the builders set forth in U.S. Patent 3,308,067, Diehl, incorporated herein by reference. Examples of such materials include the water-soluble salts of homo- and co-polymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid, and methylenemalononic acid.

Other suitable polymeric polycarboxylates are the polyacetal carboxylates described in U.S. Pat. No. 4,144,226, issued Mar. 13, 1979 to Crutchfield et al, and U.S. Pat. No. 4,246,495, issued Mar. 27, 1979 to Crutchfield et al. These polyacetal carboxylates can be prepared by bringing together under polymerization conditions an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a surfactant.

Preferred builders herein are polycarboxylic acids, especially citric acid, which preferably are used at a level of from 5% to 10% by weight, and sodium acid pyrophosphate, which preferably is used at a level of from 5% to 15% by weight. Such materials function as both builder and acid source to adjust pH to the desired range.

Detergent Adjuvants

The detergent compositions herein can contain all manner of additional materials, detergent adjuvants, commonly found in laundering and cleaning compositions. For example, the compositions can contain thickeners and soil-suspending agents such as carboxymethylcellulose and the like. Various enzymes, enzyme stabilizers, suds suppressors, perfumes, optical bleaches, fillers, anticaking agents, fabric softeners and the like can be present in the compositions to provide the usual benefits occasioned by the use of such materials in detergent compositions.

The compositions herein are essentially free of oxygen bleaching agents, since if they are present, there is no need for the chlorine scavenger. Similarly, there should be no chlorine bleaching agent present since the chlorine scavenger would not be effective against a large amount of available chlorine.

A finished detergent composition of this invention can contain minor amounts of materials which make the product more attractive. The following are mentioned by way of example: a tarnish inhibitor such as benzotriazole or ethylene thiourea can be added in amounts up to 2% by weight; fluorescers, perfumes and dyes, while not essential, can be added in small amounts. An alkaline material such as sodium or potassium carbonate or hydroxide can be added in minor amounts as supplementary pH adjusters. There may also be mentioned, as suitable additives: bacteriostats, bactericides, corrosion inhibitors such as soluble alkali silicates (preferably sodium silicates having an $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of from 1:1 to 2.8:1), and textile softening agents.

The compositions herein are granular laundry detergents comprising by weight:

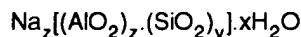
(a) from 15% to 25% of a mixture of a C_{11} - C_{13} (preferably C_{12} - C_{13}) alkylbenzene sulfonate surfactant and a C_{12} -

C₁₆ (preferably C₁₄-C₁₅) alkyl sulfate surfactant in a weight ratio of sulfonate surfactant to sulfate surfactant of from 4:1 to 1:1;

(b) from 1% to 3% of an alkali metal (preferably sodium) silicate having a molar ratio of SiO₂ to alkali metal oxide of from 1.0 to 2.4;

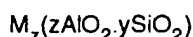
(c) from 20% to 30% of a finely divided aluminosilicate ion exchange material selected from the group consisting of:

(i) crystalline aluminosilicate material of the formula:



wherein z and y are at least 6, the molar ratio of z to y is from 1.0 to 0.5 and x is from 10 to 264, said material having a particle size diameter of from 0.1 micron to 10 microns, a calcium ion exchange capacity of at least 200 mg CaCO₃ eq./g and a calcium ion exchange rate of at least 0.130 g/l/min/g/l (2 grains Ca⁺⁺/gallon/minute/gram/gallon);

(ii) amorphous hydrated aluminosilicate material of the empirical formula:



wherein M is sodium, potassium, ammonium, or substituted ammonium, z is from 0.5 to 2 and y is 1, said material having a magnesium ion exchange capacity of at least 50 milligram equivalents of CaCO₃ hardness per gram of anhydrous aluminosilicate and a Mg⁺⁺ exchange rate of at least 0.065 g/l/min/g/l (1 grain/gallon/minute/gram/gallon); and

(iii) mixtures thereof;

(d) from 4% to 10% of citric acid;

(e) from 5% to 20% of an alkali metal (preferably sodium) carbonate;

said composition having a pH of from 7 to 9.3 at a concentration of 1% by weight in water at 20°C, and said composition having a density of from 500 to about 600 grams per liter.

Preferred aluminosilicate ion exchange material is of the formula Na₁₂[(AlO₂)₁₂(SiO₂)₁₂] · xH₂O, wherein x is from 20 to 30.

The above granular detergent compositions provide good cleaning performance due to the relatively high levels of anionic surfactants and aluminosilicate, citric acid, and carbonate builders. Despite having a density of from 500 to 600 grams per liter, the compositions have good physical properties, i.e., they are free-flowing and are readily soluble in the laundering solution. The citric acid and carbonate levels are selected to obtain the required pH range and provide additional builder function to the aluminosilicate material.

All percentages, parts and ratios herein are by weight unless otherwise specified.

The following examples illustrate the compositions herein.

EXAMPLES

Granular detergent compositions of the present invention comprise the following ingredients:

<u>Ingredient</u>	<u>Percent (Wt)</u>	
	<u>I</u>	<u>II</u>
Sodium 12.3 linear alkyl		

	benzene sulfonate	13.6	12.7
	Sodium C ₁₄ -C ₁₅ alkyl sulfate	5.8	5.4
5	Citric acid	5.5	4.9
	Zeolite A, hydrate (1-10 micron size)	26.9	27.3
10	Sodium carbonate	10.0	8.9
	Sodium silicate (1.6 ratio NaO/SiO ₂)	2.2	2.1
15	Polyethylene glycol 8000	1.4	1.3
	Sodium polyacrylate (MW 4500)	3.2	3.0
	Protease enzyme*	1.8	1.7
	Ammonium sulfate	2.0	2.0
20	Sodium sulfate	18.3	17.1
	Balance (including water, brightener, perfume, suds suppressor)	----- to 100.0 -----	
25	pH 1% aqueous solution at 20°C	8.7	8.9
	*Activity of 1.8 Anson units per gram.		

Aqueous crutcher mixes of the detergent compositions are prepared and spray-dried, except for the citric acid, enzyme, perfume, and ammonium sulfate which are admixed, so that they contain the above ingredients at the levels shown.

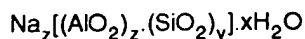
Fabrics laundered using the above compositions retain their color over time better than similar compositions not containing the chlorine scavenger or formulated to provide a higher wash pH.

Claims

1. A low or no phosphate granular laundry detergent composition characterized in that it comprises, by weight:

- (a) from 15% to 25% of a mixture of a C₁₁-C₁₃ alkylbenzene sulfonate surfactant and a C₁₂-C₁₆ alkyl sulfate surfactant in a weight ratio of sulfonate surfactant to sulfate surfactant of from 4:1 to 1:1;
- (b) from 1% to 3% of an alkali metal silicate having a molar ratio of SiO₂ to alkali metal oxide of from 1.0 to 2.4;
- (c) from 20% to 30% of a finely divided aluminosilicate ion exchange material selected from the group consisting of:

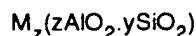
(i) crystalline aluminosilicate material of the formula:



wherein z and y are at least 6, the molar ratio of z to y is from 1.0 to 0.5 and x is from 10 to 264, said material having a particle

size diameter of from 0.1 micron to 10 microns, a calcium ion exchange capacity of at least 200 mg CaCO₃ eq./g and a calcium ion exchange rate of at least 0.130 g/l/min/g/l (2 grains Ca⁺⁺/gallon/minute/gram/gallon);

(ii) amorphous hydrated aluminosilicate material of the empirical formula:



wherein M is sodium, potassium, ammonium, or substituted ammonium, Z is from 0.5 to 2 and y is 1, said material having a magnesium ion exchange capacity of at least 50 milligram equivalents of CaCO₃ hardness per gram of anhydrous aluminosilicate and a Mg⁺⁺ exchange rate of at least 0.065 g/l/min/g/l (1 grain/gallon/minute/gram/gallon); and

(iii) mixtures thereof;

(d) from 4% to 10% of citric acid;

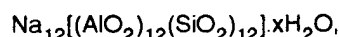
(e) from 5% to 20% of an alkali metal carbonate; said composition having a pH of from 7 to 9.3 at a concentration of 1% by weight in water at 20°C, and said composition having a density of from 500 to 600 grams per liter.

2. The composition of Claim 1 wherein the sulfonate surfactant is sodium C₁₂-C₁₃ linear alkylbenzene sulfonate and the sulfate surfactant is sodium C₁₄-C₁₅ linear alkyl sulfate.

3. The composition of any one of the preceding claims comprising from 18% to 23% of the sulfonate and sulfate surfactants, in a weight ratio of sulfonate surfactant to sulfate surfactant of 2:1.

4. The composition of any one of the preceding claims wherein the alkali metal silicate is sodium silicate having a molar ratio of SiO₂ to alkali metal oxide of from 1.4 to 2.0.

5. A composition according to any one of the preceding claims wherein the aluminosilicate ion exchange material is of the formula



wherein x is from 20 to 30.

6. A composition according to any one of the preceding claims comprising from 22% to 28% of the aluminosilicate ion exchange material.

7. A composition according to any one of the preceding claims comprising from 5% to 8% of citric acid.

8. A composition according to any one of the preceding claims comprising from 8% to 12% of sodium carbonate.

9. The composition of any one of the preceding claims wherein said composition has a pH of from 8 to 9.1, preferably from 8.5 to 9.0, at a concentration of 1% by weight in water at 20°C.

10. The composition of any one of the preceding claims which is substantially free of phosphate builder materials.

Revendications

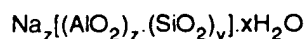
1. Composition détergente granulaire pour le linge à faible, voire aucune teneur en phosphate, caractérisée en ce qu'elle comprend, en poids :

(a) de 15 à 25% d'un mélange d'un tensioactif à base d'alkyl (en C₁₁-C₁₃) benzène-sulfonate et d'un tensioactif à base de sulfate d'alkyle (en C₁₂-C₁₆), dans un rapport pondéral du tensioactif à base de sulfonate au tensioactif à base de sulfate de 4:1 à 1:1 ;

(b) de 1 à 3% d'un silicate de métal alcalin ayant un rapport molaire de SiO₂ à l'oxyde de métal alcalin de 1,0 à 2,4 ;

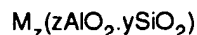
(c) de 20 à 30% d'un produit à échange d'ions aluminosilicate finement divisé choisi dans le groupe formé par :

(i) les produits à base d'aluminosilicates cristallins de formule :



dans laquelle z et y valent au moins 6, le rapport molaire de z à y est de 1,0 à 0,5 et x est de 10 à 264, lesdits produits ayant un diamètre granulométrique de 0,1 micron à 10 microns, une capacité d'échange d'ions calcium d'au moins 200 mg en éq./g de CaCO_3 et un taux d'échange d'ions calcium d'au moins 0,130 g/l/mn/g/l (2 grains Ca^{++} /gallon/minute/gramme/gallon);

(ii) les produits à base d'aluminosilicates amorphes hydratés de formule empirique :



dans laquelle M est un atome de sodium ou potassium, ou un reste ammonium ou ammonium substitué, z est de 0,5 à 2 et y est 1, lesdits produits ayant une capacité d'échange d'ions magnésium d'au moins 50 milligrammes en équivalents de dureté CaCO_3 par gramme d'aluminosilicate anhydre et un taux d'échange d'ions magnésium Mg^{++} d'au moins 0,065 g/l/mn/g/l (1 grain/gallon/minute/gramme/gallon) ; et

(iii) des mélanges de ceux-ci ;

(d) de 4 à 10% d'acide citrique ;

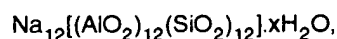
(e) de 5 à 20% d'un carbonate de métal alcalin; ladite composition ayant un pH de 7 à 9,3 à une concentration de 1% en poids dans une eau à 20°C, et ladite composition ayant une densité de 500 à 600 grammes par litre.

2. Composition selon la revendication 1, dans laquelle le tensioactif à base de sulfonate est un alkylbenzène-sulfonate de sodium linéaire en C_{12} - C_{13} et le tensioactif à base de sulfate est un alkyl-sulfate de sodium linéaire en C_{14} - C_{15} .

3. Composition selon l'une quelconque des revendications précédentes comprenant de 18 à 23% de tensioactifs à base de sulfonate et de sulfate, dans un rapport pondéral du tensioactif à base de sulfonate au tensioactif à base de sulfate de 2:1.

4. Composition selon l'une quelconque des revendications précédentes, dans laquelle le silicate de métal alcalin est un silicate de sodium ayant un rapport molaire de SiO_2 à l'oxyde de métal alcalin de 1,4 à 2,0.

5. Composition selon l'une quelconque des revendications précédentes, dans laquelle le produit à échange d'ions aluminosilicate est de formule :



dans laquelle x est de 20 à 30.

6. Composition selon l'une quelconque des revendications précédentes comprenant de 22 à 28% de produit à échange d'ions aluminosilicate.

7. Composition selon l'une quelconque des revendications précédentes comprenant de 5 à 8% d'acide citrique.

8. Composition selon l'une quelconque des revendications précédentes comprenant de 8 à 12% de carbonate de sodium.

9. Composition selon l'une quelconque des revendications précédentes, dans laquelle ladite composition a un pH de 8 à 9,1, de préférence de 8,5 à 9,0, à une concentration de 1% en poids dans une eau à 20°C.

10. Composition selon l'une quelconque des revendications précédentes qui est essentiellement exempte de produits d'activation à base de phosphate.

Patentansprüche

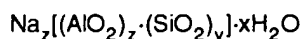
1. Granulatförmige Wäschewaschmittelzusammensetzung ohne Phosphat oder mit geringem Phosphatgehalt, dadurch gekennzeichnet, daß sie, bezogen auf Gewicht:

(a) 15 bis 25 % einer Mischung aus einem C_{11} - C_{13} -Alkylbenzolsulfonat-Tensid und einem C_{12} - C_{16} -Alkylsulfat-Tensid in einem Gewichtsverhältnis von Sulfonat-Tensid zu Sulfat-Tensid von 4:1 bis 1:1;

(b) 1 bis 3 % eines Alkalimetallsilikats mit einem Molverhältnis von SiO_2 zu Alkalimetalloxid von 1,0 bis 2,4;

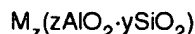
(c) 20 bis 30 % eines fein verteilten Aluminosilikat-Ionenaustauschermaterials, gewählt aus der

(i) kristallines Aluminosilikatmaterial der Formel:



worin z und y mindestens 6 sind, das Molverhältnis von z zu y 1,0 bis 0,5 beträgt und x 10 bis 264 ist, wobei dieses Material einen Teilchengrößendurchmesser von 0,1 µm bis 10 µm, eine Calciumionen-Austauschkapazität von mindestens 200 mg CaCO₃ eq./g und eine Calciumionen-Austauschrate von mindestens 0,130 g/l/min/g/l (2 grains Ca++/gallon/minute/gram/gallon) aufweist;

(ii) amorphes hydratisiertes Aluminosilikatmaterial der empirischen Formel:



worin M Natrium, Kalium, Ammonium oder substituiertes Ammonium ist, z 0,5 bis 2 ist und y 1 ist, wobei dieses Material eine Magnesiumionen-Austauschkapazität von mindestens 50 Milligrammäquivalenten CaCO₃-Härte pro Gramm wasserfreies Aluminosilikat und eine Mg⁺⁺-Austauschrate von mindestens 0,065 g/l/min/g/l (1 grain/gallon/minute/gram/gallon) aufweist; und

(iii) Mischungen hiervon umfassenden Gruppe;

(d) 4 bis 10 % Zitronensäure;

(e) 5 bis 20 % eines Alkalimetallcarbonats umfaßt;

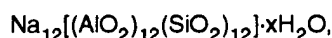
wobei die Zusammensetzung einen pH von 7 bis 9,3 bei einer Konzentration von 1 Gew.-% in Wasser bei 20°C aufweist und die Zusammensetzung eine Dichte von 500 bis 600 Gramm pro Liter besitzt.

2. Zusammensetzung nach Anspruch 1, wobei das Sulfonat-Tensid Natrium-lineares C₁₂-C₁₃-Alkylbenzolsulfonat ist und das Sulfat-Tensid Natriumlineares C₁₄-C₁₅-Alkylsulfat ist.

3. Zusammensetzung nach Anspruch 1 oder 2, umfassend 18 bis 23 % des Sulfonat- und Sulfat-Tensids in einem Gewichtsverhältnis von Sulfonat-Tensid zu Sulfat-Tensid von 2:1.

4. Zusammensetzung nach einem der vorangehenden Ansprüche, wobei das Alkalimetallsilikat Natriumsilikat mit einem Molverhältnis von SiO₂ zu Alkalimetalloxid von 1,4 bis 2,0 ist.

5. Zusammensetzung nach einem der vorangehenden Ansprüche, wobei das Aluminosilikat-Ionenaustauschermaterial der Formel



entspricht, worin x 20 bis 30 ist.

6. Zusammensetzung nach einem der vorangehenden Ansprüche, umfassend 22 bis 28 % des Aluminosilikat-Ionenaustauschermaterials.

7. Zusammensetzung nach einem der vorangehenden Ansprüche, umfassend 5 bis 8 % Zitronensäure.

8. Zusammensetzung nach einem der vorangehenden Ansprüche, umfassend 8 bis 12 % Natriumcarbonat.

9. Zusammensetzung nach einem der vorangehenden Ansprüche, wobei die Zusammensetzung einen pH von 8 bis 9,1, vorzugsweise von 8,5 bis 9,0, bei einer Konzentration von 1 Gew.-% in Wasser bei 20°C aufweist.

10. Zusammensetzung nach einem der vorangehenden Ansprüche, welche im wesentlichen frei an Phosphat-Buildermaterialien ist.